

CHAPTER 7

COVALENT BONDS AND MOLECULAR STRUCTURE

Chapter Learning Goals

- Section 7.1** Determine the H–H bond length from a plot of potential energy versus internuclear distance for the hydrogen molecule. Use atomic radii to estimate bond length.
- Section 7.2** Define bond dissociation energy, D . Give a range of bond dissociation energies for common bonds.
- Section 7.3** From a list of compounds, predict which are ionic and which are molecular.
- Section 7.4** Using only the periodic table, predict which of two elements is more electronegative. Using only the periodic table, predict whether a given bond is ionic, polar covalent, or nonpolar covalent. Using a table of electronegativities, predict which of two bonds is expected to be more polar.
- Section 7.5** Write Lewis symbols for atoms, and tell how many electrons must be shared to enable the atom to achieve a completed valence shell. Give the symbol of the noble gas with the same number of valence electrons. Draw electron-dot structures for simple molecules.
- Section 7.6** Draw electron-dot structures for polyatomic molecules and ions, recognizing when multiple bonding is needed. For each atom in an electron-dot structure, give the number of bonded electron pairs and the number of nonbonded electron pairs. For a given electron-dot structure, give the number of single bonds, double bonds, and triple bonds. Give the bond order of each bond.
- Section 7.7** Draw electron-dot structures for polyatomic molecules and ions, recognizing when resonance structures are needed. Give the bond order of each bond in an electron-dot structure that requires resonance structures.
- Section 7.8** Calculate the formal charge on each atom in a molecule. Determine the formal charge on each atom in a resonance structure, and use the formal charges to select the best resonance structure.
- Section 7.9** Use the VSEPR model to predict the geometries of molecules and polyatomic ions, including those with more than one central atom.
- Section 7.10** For molecules and polyatomic ions, sketch and identify the orbitals used by each atom to form bonds. Show which orbital overlaps result in σ bonds and which result in π bonds.
- Section 7.11** Describe the formation of sp^3 hybrid orbitals, and give the spatial orientation of the four sp^3 hybrid orbitals. Describe the bonding in a polyatomic molecule, and tell which atoms use of sp^3 hybrid orbitals to form bonds.
- Section 7.12** Describe the formation of sp and sp^2 hybrid orbitals, and give the spatial orientation of the two sp hybrid orbitals and the three of sp^2 hybrid orbitals, and identify the orbitals involved in bonding. Describe the bonding in a polyatomic molecule, and tell what kinds of orbitals on each atom overlap to form bonds.
- Section 7.13** Identify bonding and antibonding molecular orbitals. Sketch a molecular orbital diagram for a diatomic molecule. Use the molecular orbital diagram to determine the number of unpaired electrons and to calculate the bond order of the molecule described.

Lecture Outline

7.1. The Covalent Bond

- A. Formation of a covalent bond
 - 1. Two atoms come close together, and electrostatic interactions develop
 - a. Nuclei repel each other; electrons repel each other
 - b. Each nucleus attracts the same electrons; electrons attract both nuclei
 - 2. If attractive forces > repulsive forces; then covalent bond formed
- B. Distance between the two atoms affects the magnitude of attractive and repulsive forces.
 - 1. Bond length – optimum point where net attractive forces maximized
 - a. Each covalent bond has a characteristic length that leads to maximum stability.
 - b. Can predict from atomic radii

7.2. Strengths of Covalent Bonds

- A. Formation of covalent bonds leads to lower energy.
- B. Bond dissociation energy, D (units in KJ/mol)
 - 1. Amount of energy necessary to break a chemical bond in an isolated gaseous-state molecule
 - 2. Only positive values possible
 - 3. When a bond forms, $\Delta H = -D$
 - a. Bond breaking requires energy (D)
 - b. Bond formation releases energy ($-D$)
- C. Bonds between the same pairs of atoms usually have similar bond dissociation energies.

7.3. A Comparison of Ionic and Covalent Compounds

- A. Ionic compounds
 - 1. High-melting solids.
 - 2. Must overcome every ionic attraction in the entire crystal to dissociate
- B. Covalent compounds
 - 1. Low-melting solids, liquids, or even gases
 - 2. Bonds within individual molecule may be very strong
 - 3. Attractive forces between different molecules (intermolecular forces) are relatively weak.

7.4. Polar Covalent Bonds: Electronegativity

- A. Ionic and covalent bonds – extremes of a continuous spectrum of possibilities
- B. Polar covalent bonds – bonding electrons attracted somewhat more strongly by one atom in a bond
 - 1. Electrons not completely transferred
 - 2. More electronegative atom: δ^- (δ represents partial charge formed.)
 - 3. Less electronegative atom: δ^+
- C. Electronegativity (EN) – ability of an atom in a molecule to attract shared electrons in a bond
 - 1. Metallic elements – low electronegativities
 - 2. Halogens and other elements in upper right-hand corner of periodic table – high electronegativities.
- D. Predicting bond polarity – general rules of thumb
 - 1. Atoms with similar electronegativities ($\Delta EN \leq 0.4$) – form nonpolar bonds
 - 2. Atoms whose electronegativities differ by more than two ($\Delta EN > 2$) – form ionic bonds
 - 3. Atoms whose electronegativities differ by less than two ($\Delta EN < 2$) – form polar covalent bonds

7.5. Electron-Dot Structures

- A. Electron-dot structure – atom's valence-electron distribution in a molecule
 - 1. Lewis Structure – Simplified tool for understanding the chemistry and configuration of main group elements.
- B. Maximum stability when s and p subshells filled for each atom in a molecule
- C. Electron-dot structures for elements
 - 1. Electrons represented by dots around element symbol
 - a. One to each side until all four sides occupied
 - b. Then pair dots until all valence-shell electrons used
 - c. Note: pairing of dots does not correspond to pairing of electrons in electron configuration.
- D. Simple molecules of second-period main-group elements – textbook Table 7.3

1. Octet rule used to determine number of covalent bonds formed by an element
 2. Unpaired electrons form bonds – number of unpaired electrons determines number of bonds formed by atom.
 3. Electrons shared until each atom surrounded by four pairs of electrons (an octet)
 4. Lone pairs (nonbonded pairs) – electron pairs not used in bonding
 5. Bonding pairs – electrons shared in bond formation
- E. Multiple covalent bonds – sometimes more than one pair of electrons shared
1. Shorter and stronger than single bonds.
 2. Double bond – two pairs of electrons shared
 3. Triple bond – three pairs of electrons shared
 4. Bond order – number of electron pairs shared
 - a. Bond order = 1
 - i. Single bond
 - ii. Two electrons shared
 - b. Bond order = 2
 - i. Double bond
 - ii. Four electrons shared
 - c. Bond order = 3
 - i. Triple bond
 - ii. Six electrons shared
- F. Coordinate covalent bonds – typical of transition metals complexes
1. Two electrons (a lone pair) donated by one atom to another atom in bond formation
 2. Second atom has vacant (unfilled) valence orbital
 3. Often formed by N, O, P, and S
 4. Once formed, coordinate bonds behave the same as ordinary covalent bonds
 5. Coordinate bonds do not change the overall charge of the transition metal complex or polyatomic ion.

7.6. Electron-Dot Structures of Polyatomic Molecules

- A. Compounds of second-row elements: C, H, N, O
1. Octet rule almost always applies
 2. Easy to predict number of bonds formed by each element – similar to above
 3. Number of bonds formed equals number of unpaired dots in the Lewis formula
 4. Indicate covalent single bond by a single line
 - a. Double bond – two lines
 - b. Triple bond – three lines
- B. Compounds with elements beyond the second row
1. Third period and lower elements larger than second-period elements
 2. Larger size allows bonds to more than four atoms
 3. “Expanded octet”
- C. Except for hydrogen, all terminal atoms will always have complete octets
- D. General method for drawing electron-dot structures – textbook pages 236

7.7. Electron-Dot Structures and Resonance

- A. Sometimes more than one electron-dot structure needed for molecular description
- B. Resonance hybrid – average of various possible electron-dot structures for a molecule
1. Resonance indicated by straight double-headed arrows (\leftrightarrow) joining resonance structures
 2. Resonance structures differ only in valence electron placement

7.8. Formal Charges

- A. Result of electron bookkeeping
1. Formal charge = (number of valence electrons in free atom) – $1/2$ (number of bonding electrons) – (number of nonbonding electrons)
 2. Sum of formal charges on all atoms = overall charge on the molecule
- B. Use to evaluate relative importance of different resonance structures
1. Structures with smallest formal charges more stable
 2. The best resonance structure has
 - a. formal charges as close to zero as possible, and

- b. a negative formal charge on the most electronegative element or a positive formal charge on the least electronegative element.

7.9. Molecular Shapes: The VSEPR Model

- A. Molecular shape – determined by numbers of valence electrons around atoms
- B. Valence-shell electron-pair repulsion model – predicts approximate molecular shape
 - 1. Bonded and lone electrons occupy charge clouds
 - 2. Count the number of charge clouds surrounding atom
 - 3. Geometry based on number of charge clouds and relative positions of substituent nuclei
 - a. Charge clouds – stay as far away as possible from each other due to electrostatic repulsion
 - b. Textbook Table 7.4

7.10. Valence Bond Theory

- A. Easily visualized orbital picture of how electron pairs become shared by the overlap of atomic orbitals in a covalent bond
- B. Orbital overlap – bond formation
 - 1. Greater the overlap, stronger the bond
 - 2. Singly-occupied valence orbital on one atom overlaps a singly occupied valence orbital on another atom
- C. For orbitals other than s orbitals, orbitals used in bond formation have directionality
- D. Each bonded atom maintains its own orbital but shares electrons

7.11. Hybridization and sp^3 Hybrid Orbitals

- A. Hybrid orbitals – combination of wave functions for atomic orbitals that forms a new set of equivalent wave functions. Hybrid orbital sets have the same geometry as the electron clouds predicted by VSEPR model
- B. Combine one s with three p – form four equivalent new orbitals, each named sp^3
 - 1. Each hybrid
 - a. Two lobes
 - b. One larger than the other
 - 2. Four large lobes point toward corners of a tetrahedron
 - 3. Bonds formed with sp^3 orbitals are very strong
- C. A tetrahedral arrangement of charge clouds always implies sp^3 hybridization.

7.12. Other Kinds of Hybrid Orbitals

- A. Geometries related to hybrid orbitals used
 - 1. Textbook Table 7.5
 - 2. Each electron-cloud geometry has a corresponding set of hybrid orbitals
- B. Sigma (σ) bond
 - 1. Bond formed by head-on overlap
 - 2. Has shared electrons centered about the axis between the two nuclei
- C. Pi (π) bond
 - 1. Bond formed by side-by-side overlap
 - 2. Has shared electrons occupying a region above and below a line connecting the two nuclei

7.13. Molecular Orbital Theory: The Hydrogen Molecule

- A. Molecular orbital model
 - 1. More complex bonding model than valence bond
 - 2. Considers molecule as a whole rather than concentrating on individual atoms
 - 3. Sometimes bonding description offers better agreement with experimental observations
- B. Atomic orbital – wave function whose square gives probability of finding the electron within a given region of space in an atom
- C. Molecular orbital – a wave function whose square gives probability of finding the electron within a given region of space in a molecule
 - 1. Specific energy level
 - 2. Specific shape
 - 3. Occupied by a maximum of two electrons with opposite spins
- D. Orbital interactions in molecular orbital theory
 - 1. Additive interaction
 - a. For H_2 – formation of egg-shaped molecular orbital

- b. Denoted σ
- c. Lower in energy than the two isolated $1s$ orbitals
- d. Bonding molecular orbital (MO)
 - i. Electrons in bonding MO spend most time in region between the two nuclei
 - ii. Bonds atoms together
- 2. Subtractive interaction.
 - a. For H_2 – formation of molecular orbital that has a node between the two atoms
 - b. Denoted σ^*
 - c. Higher in energy than the two isolated $1s$ orbitals
 - d. Antibonding molecular orbital
 - i. Electrons in antibonding MO do not occupy central region between the nuclei
 - ii. Don't contribute to bonding
- E. Bond order = $1/2(\text{number of bonding electrons} - \text{number of antibonding electrons})$
- F. Number of molecular orbitals formed = the number of atomic orbitals combined
- G. Key ideas of molecular orbital theory – see textbook

7.14. Molecular Orbital Theory of Other Diatomic Molecules

- A. Paramagnetic – substances with unpaired electrons are attracted by magnetic fields
- B. Diamagnetic – substances whose electrons are all spin-paired
- C. Molecular orbital of O_2
 - 1. Two $2s$ orbitals interact to form σ_{2s} and σ_{2s}^* molecular orbitals
 - 2. Two $2p$ orbitals on the internuclear axis
 - a. Interact head-on
 - b. Form σ_{2p} and σ_{2p}^* molecular orbitals
 - 3. Remaining $2p$ orbitals perpendicular to the internuclear axis
 - a. Interact in sideways manner
 - b. Form π_{2p} and π_{2p}^* molecular orbitals
 - 4. Energy levels of molecular orbitals – textbook Figure 7.18
- D. Molecular orbital diagrams require some experience to generate.

7.15. Combining Valence Bond Theory and Molecular Orbital Theory

- A. Molecules with resonance structures
 - 1. σ -bond framework
 - a. Localized
 - b. Describe with valence bond theory
 - 2. π -bond framework
 - a. Delocalized
 - b. Describe with molecular orbital theory